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THERMAL STABILITY AND CRYSTALLIZATION  
OF TRANSITION METAL-BORON  
METALLIC GLASSES

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METAL-BORON METALLIC GLASSES

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## АННОТАЦИЯ

Методами калориметрии, рентгеновской дифракции и мессбауэровской спектроскопии изучалась кристаллизация металлических стекол  $(\text{Fe}_{1-x}^{\text{TM}})_x\text{B}_{25-y}$  ( $\text{TM} = \text{Co}, \text{Ni}$ ) в области состава  $0 < x < 1$  и  $0 < y < 10$ . Определены кристаллические фазы и изучена их роль в изменении ближнего порядка аморфных сплавов.

## KIVONAT

$(\text{Fe}_{1-x}^{\text{TM}})_x\text{B}_{25-y}$  ( $\text{TM} = \text{Co}, \text{Ni}$ ) üvegek kristályosodását vizsgáltuk az  $0 < x < 1$  és  $0 < y < 10$  összetétel-tartományban kalorimetria, röntgendiffrakció és Mössbauer spektroszkópia segítségével. Meghatároztuk a kristályos fázisokat és megvizsgáltuk ezek szerepét az amorf ötvözetek rövidtávu rendjének változásában.



## ABSTRACT

The crystallization of  $(\text{Fe}_{1-x}\text{TM}_x)_{75+y}\text{B}_{25-y}$  - TM = Co and Ni - glasses are investigated in the  $0 < x < 1$ ,  $0 < y < 10$  composition range by calorimetry, X-ray diffraction and Mössbauer spectroscopy. The crystalline phases are identified and their relation to possible changes in the chemical short range order of these amorphous alloys is discussed.

## INTRODUCTION

The study of chemical and topological short range order (SRO) is one of the most important questions in the research of metallic glasses. In the Fe-B system it was shown [1] that the Fe environments in the glassy phase are remarkably similar to those of the tetragonal  $\text{Fe}_3\text{B}$  (isostructural to  $\text{Fe}_3\text{P}$ ) intermetallic compound which is formed during the crystallization. As the structure of  $\text{Ni}_3\text{B}$  and  $\text{Co}_3\text{B}$  (cementite type, orthorhombic) is different from  $\text{Fe}_3\text{B}$ , one would expect changes in the short range order of Fe-B glasses due to the replacement of Fe by Co or Ni.

In this paper the crystallization of  $(\text{Fe,Ni})\text{B}$  and  $(\text{Fe,Co})\text{B}$  glasses is investigated. The effect of composition on the thermal stability of the amorphous alloys and on the structure of the stable and metastable crystalline phases has been analyzed.

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## EXPERIMENTAL

The crystallization of (Fe,Ni)B and (Fe,Co)B glasses has been investigated by a Perkin-Elmer DSC-2 differential scanning calorimeter. The structure of the crystalline phases has been determined by X-ray diffraction and Mössbauer spectroscopy. The results of transmission electron microscopy studies are published separately [2].

## RESULTS AND DISCUSSION

The crystallization temperatures of  $(\text{Fe}_{1-x}\text{Ni}_x)_{75}\text{B}_{25}$ ,  $(\text{Fe}_{1-x}\text{Co}_x)_{75}\text{B}_{25}$  and  $(\text{Fe}_{1-x}\text{Co}_x)_{80}\text{B}_{20}$  glasses are plotted on Fig. 1-3. The results for  $(\text{Fe}_{1-x}\text{Ni}_x)_{80}\text{B}_{20}$  and  $(\text{Fe}_{1-x}\text{Ni}_x)_{85}\text{B}_{15}$  glasses were published previously [3].

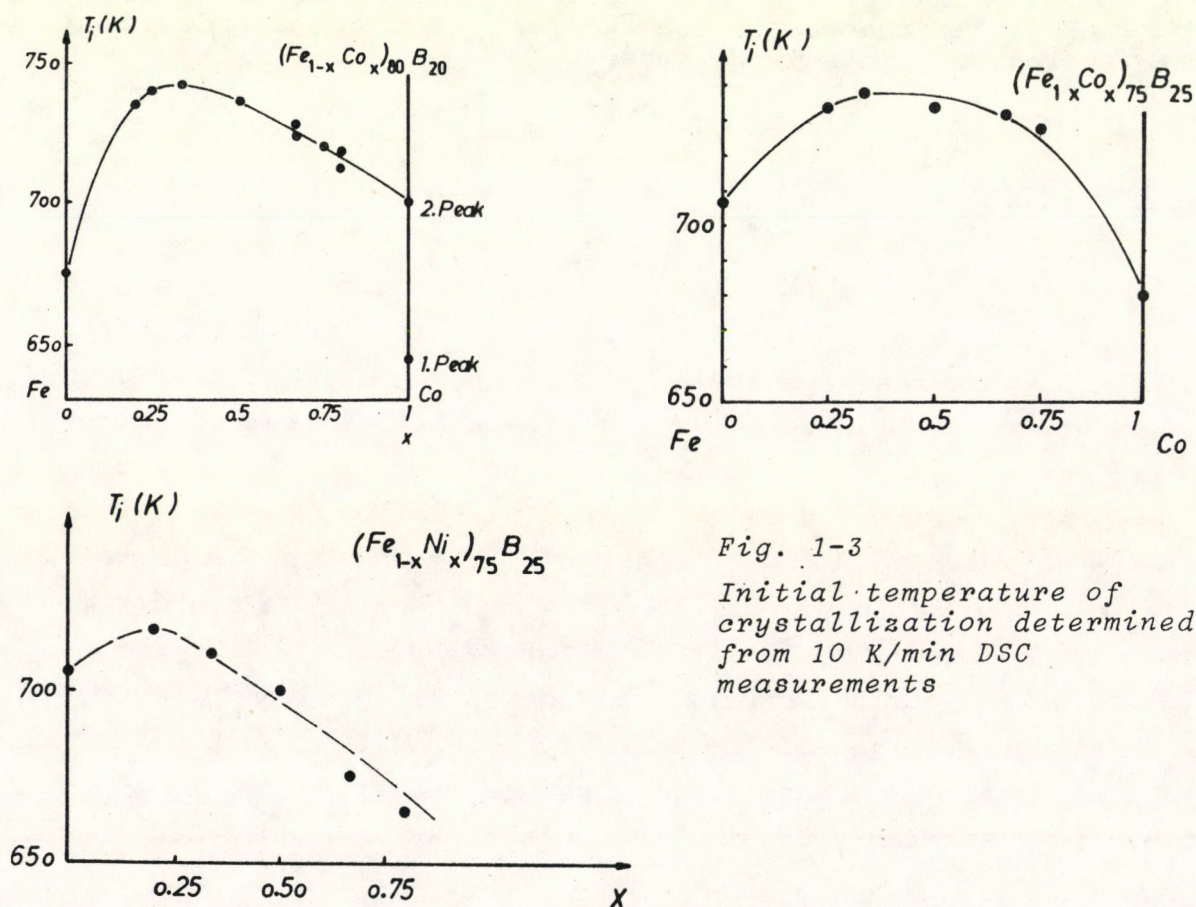


Fig. 1-3

Initial temperature of crystallization determined from 10 K/min DSC measurements



All of the results indicate that crystallization temperature of the ternary glasses is somewhat increasing compared to that of the binaries. This is expected as a result of the stabilizing role of the entropy of mixing. The increase is significantly smaller in the (Fe,Ni)B system than in (Fe,Co)B. It is connected with differences in binding energies which influence thermal stability by changing atomic mobility. The energy factor can even overcome the entropy term resulting in the decrease of crystallization e.g. at the substitution of C for B [4] or Cu, Pd and Pt for Fe [5] in Fe-B glasses.

The stability of binary Co-B glasses is lower than that of Fe-B. It is reflected in the appearance of double stage crystallization in  $\text{Co}_{80}\text{B}_{20}$  glass, where the first step is identified by diffraction measurements as Co precipitation, while the second peak which appears in the temperature range expected from the ternaries is the formation of orthorhombic  $\text{Co}_3\text{B}$ .

The phases appearing during the crystallization of (Fe,Ni)B and (Fe,Co)B glasses were investigated by X-ray diffraction and Mössbauer spectroscopy. The structures have been identified as  $\text{Fe}_{1-x}\text{TM}_x$ ,  $(\text{Fe}_{1-x}\text{TM}_x)_3\text{B}$  and  $(\text{Fe}_{1-x}\text{TM}_x)_2\text{B}$  where TM=Co and Ni. All of the  $(\text{Fe}_{1-x}\text{TM}_x)_2\text{B}$  compounds are isostructural having a tetragonal structure of the  $\text{CuAl}_2$  type [6]. The crystal structure of  $(\text{Fe}_{1-x}\text{TM}_x)_3\text{B}$  intermetallic compounds changes with composition. The metastable  $\text{Fe}_3\text{B}$  (which decomposes to  $\alpha\text{-Fe}$  and  $\text{Fe}_2\text{B}$  at high temperatures) is isostructural [7] to the tetragonal  $\text{Fe}_3\text{P}$ . It has three crystallographically inequivalent Fe sites with 2B, 3B and 4B nearest neighbours, their ratio is 1:1:1.  $\text{Ni}_3\text{B}$  and  $\text{Co}_3\text{B}$  are orthorhombic [6], isostructural to cementite ( $\text{Fe}_3\text{C}$ ). It has two crystallographically inequivalent transition metal sites with 2B and 3B nearest neighbours in 1:2 ratio. The corresponding Mössbauer spectra are shown in [8]. The  $\text{Fe}_{1-x}\text{Ni}_x$  and  $\text{Fe}_{1-x}\text{Co}_x$  alloys have b.c.c. structure in the  $0 \leq x \leq 0.3$  and  $0 \leq x \leq 0.75$  concentration range, respectively for Ni and Co. At the Ni or Co rich side the structure is f.c.c. or h.c.p.

The Mössbauer spectra of crystallized  $(\text{Fe}_{1-x}\text{Ni}_x)_{80}\text{B}_{20}$  samples are shown on Fig. 4. The outer lines correspond to the precipitated  $\text{Fe}_{1-x}\text{Ni}_x$  alloy. The spectra at low Ni content ( $x \leq 0.38$ ) show the multiple-peak structure which is characteristic to the three



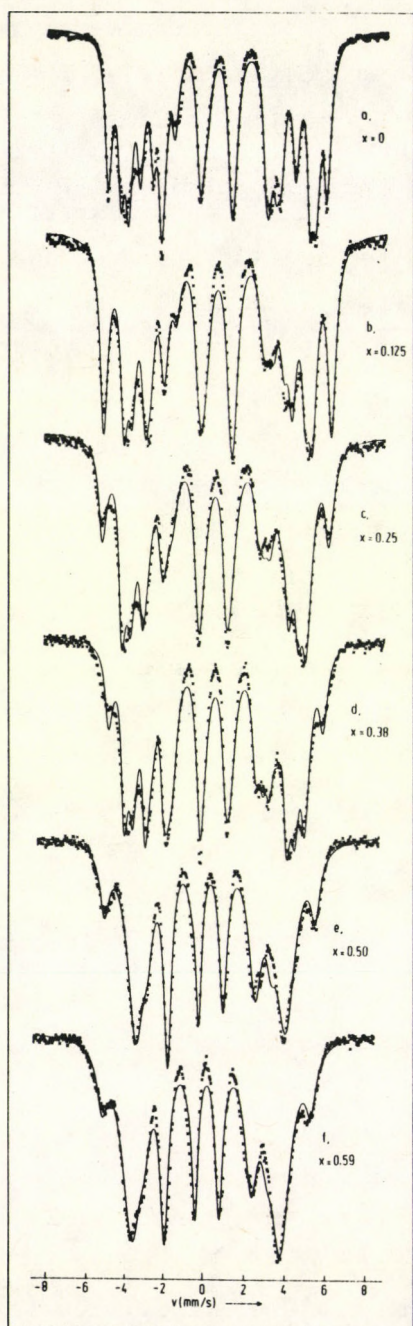


Fig. 4. Mössbauer spectra of crystallized  $(Fe_{1-x}Ni_x)_3B$  samples

$0 \leq x \leq 0.25$  : b.c.c. Fe-Ni and tetragonal  $(Fe, Ni)_3B$   
 $x = 0.38$  : f.c.c. Fe-Ni and tetragonal  $(Fe, Ni)_3B$   
 $0.5 \leq x \leq 0.79$  : f.c.c. Fe-Ni and orthorh.  $(Fe, Ni)_3B$  intermetallic compound

inequivalent Fe sites of the tetragonal phase. At higher Ni content ( $x \geq 0.5$ ) the orthorhombic structure appears. In all cases a distribution of the easy directions of magnetization is observed which results in a broadening of the lines. At the crystallization of the  $(Fe_{1-x}Ni_x)_{75}B_{25}$  glasses the formation of the orthorhombic  $(Fe_{1-x}Ni_x)_3B$  compound is detected for  $x \geq 0.33$  while a decomposition into  $(Fe_{1-x}Ni_x)_2B$  and  $Fe_{1-x}Ni_x$  occurs at the Fe rich side.

The average Mössbauer parameters extracted from the spectra are plotted on Fig. 5a, b and c. It is clear from these figures that average hyperfine field, quadrupole splitting and isomer shift follows a smooth curve, there are almost no changes at the tetragonal - orthorhombic boundary.

The Mössbauer parameters of the inequivalent Fe sites are shown in Fig. 6a and b. All of the hyperfine field and quadrupole splitting parameters show a uniform composition dependence which is connected with a homogeneous contraction of the lattice (from Fe to the other TM) which is observed by X-ray measurements.

Another interesting result of the Mössbauer experiments is that the distribution of Fe and Ni atoms is disordered in the tetragonal  $(Fe_{1-x}Ni_x)_3B$  intermetallic compounds.



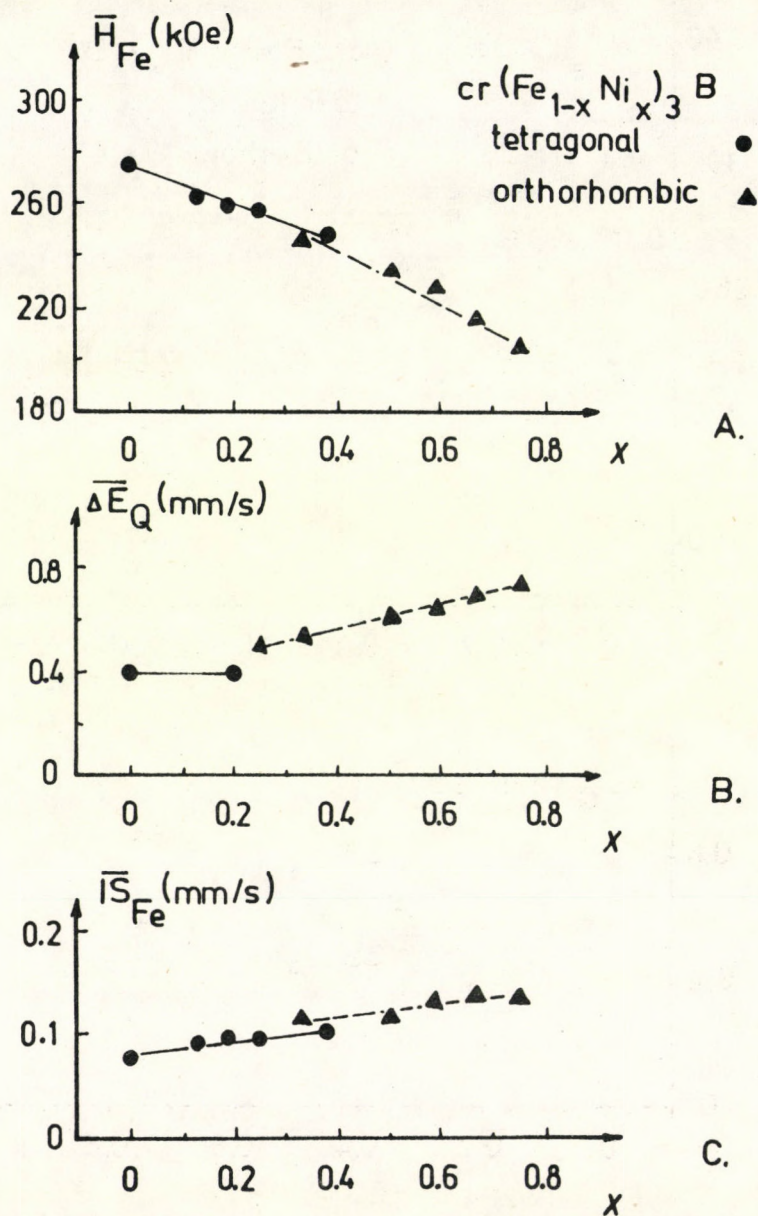


Fig. 5. Average Mössbauer parameters of  $(Fe_{1-x}Ni_x)_3B$  intermetallic compounds

A) Hyperfine field extrapolated to 0 K

B) Quadrupole splitting extrapolated to 800 K

C) Isomer shift at room temperature with respect to  $\alpha$ -Fe



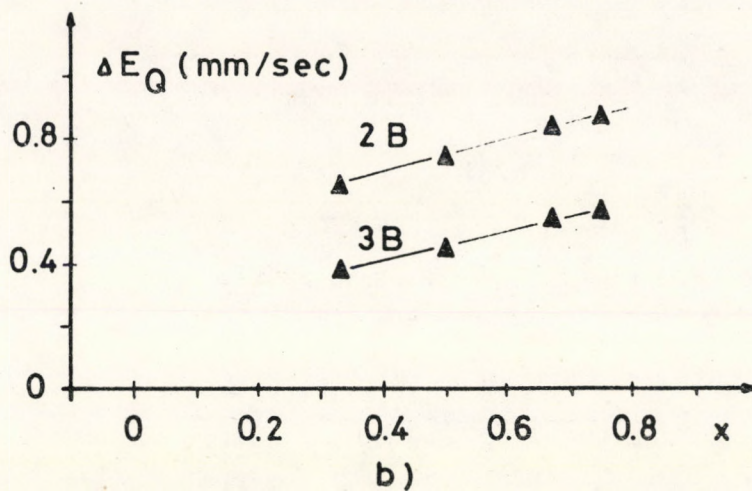
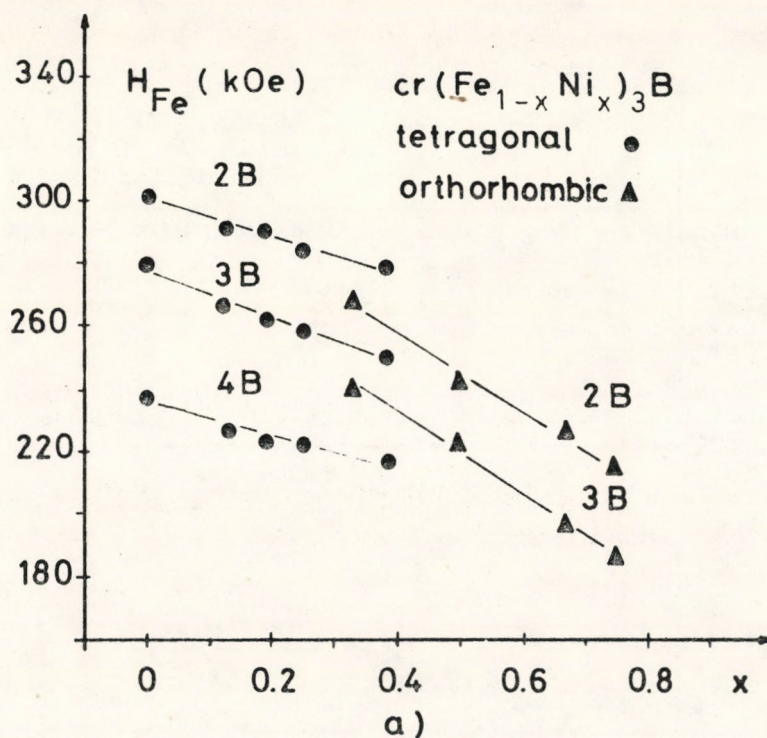


Fig. 6. Mössbauer parameters of inequivalent Fe sites in  $(Fe_{1-x}Ni_x)_3B$  intermetallic compounds. The B coordinations around Fe atoms are also indicated.

a) Hyperfine field values extrapolated to 0 K

b) Quadrupole splitting data extrapolated to 800 K



The observed relative intensities of the lines in the Mössbauer spectra are 1:1:1 in agreement with the ratio of different crystallographic sites. A similar disordered distribution is observed in the orthorhombic phase only at  $x=0.33$ , at higher Ni concentrations Fe is preferentially substituted to the sites with 2B nearest neighbours. This behaviour and the similar preference also observed in the glassy phase [8] may be explained by differences in the Fe-B and Ni-B binding as it is suggested in [9].

The crystallization of (Fe,Co)B glasses follows a similar pattern. The only difference is that off-stoichiometry - deviation of B content from 25 at.% - stabilizes the tetragonal  $(\text{Fe}_{1-x}\text{Co}_x)_3\text{B}$  phase in a somewhat larger concentration range ( $0 \leq x \leq 0.5$ ) than in  $(\text{Fe}_{1-x}\text{Ni}_x)_3\text{B}$ , where it is observed for  $0 \leq x \leq 0.38$ .

#### CONCLUSION

The most important conclusion of the present work is that the local properties of  $(\text{Fe,Ni})_3\text{B}$  intermetallic compounds change smoothly at the tetragonal-orthorhombic boundary. No drastic changes are therefore expected in the glassy phase due to the variation of short range order [8].

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